The quest for CO_2-free hydrogen – methane pyrolysis at scale

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ARPA-E Methane Cohort Kickoff, Houston, December 10, 2019

BASF – We create chemistry

Our chemistry is used in almost all industries

We combine economic success, social responsibility and environmental protection

Sales 2017: €64,457 million

EBIT 2017: €8,522 million

Employees: 115,490 (as of December 31, 2017)

6 Verbund sites and 347 other production sites

Agenda

1. Why CO_2-free hydrogen via methane pyrolysis?
2. Technological routes for methane pyrolysis
3. Summary

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1. Why CO_2-free hydrogen via methane pyrolysis?

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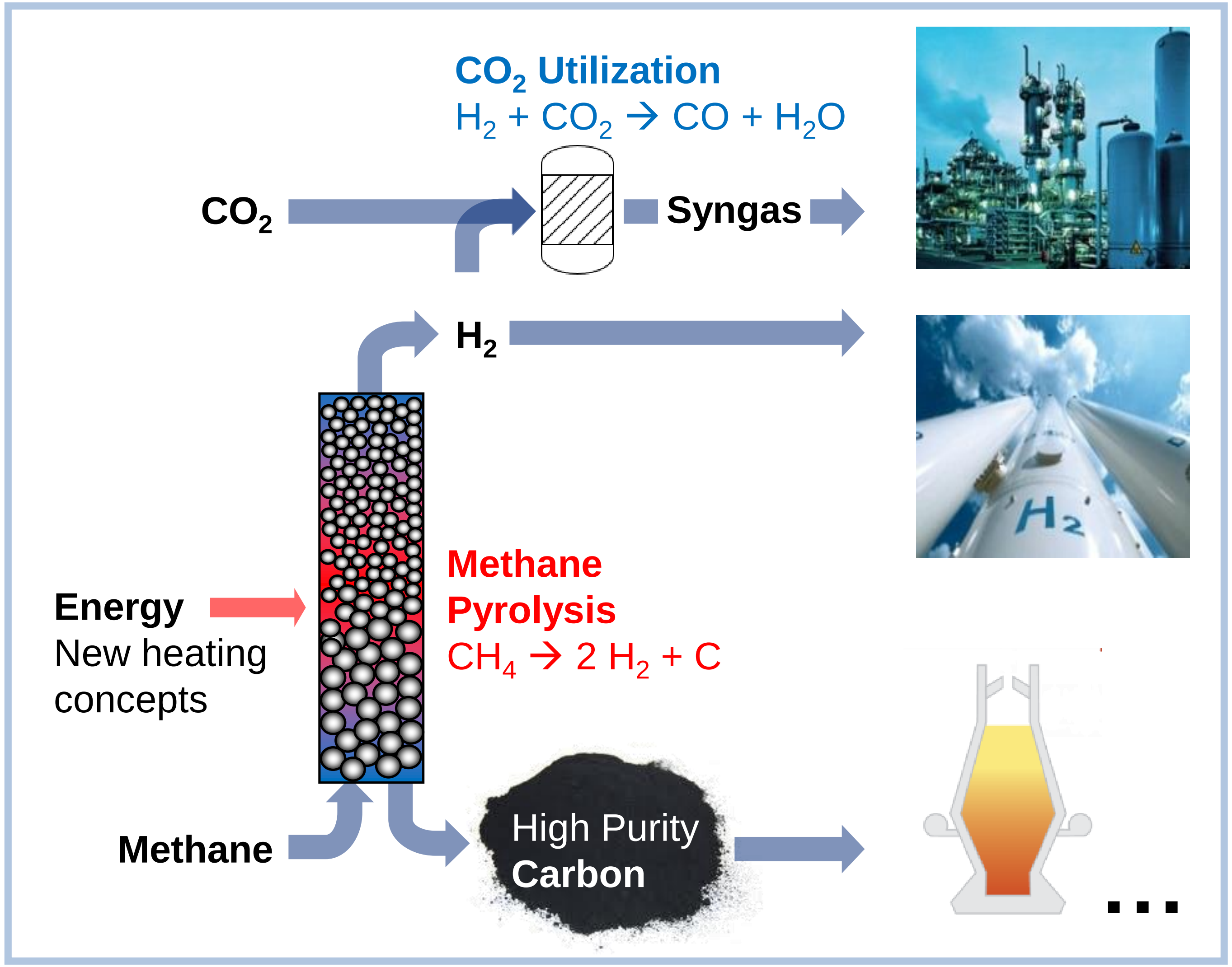
Methane pyrolysis and CO_2 activation

BMBF sponsored first project FfPaG (“fluid and solid products from gas”, 2013-2017)



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<u>Basic ideas behind FfPaG</u>

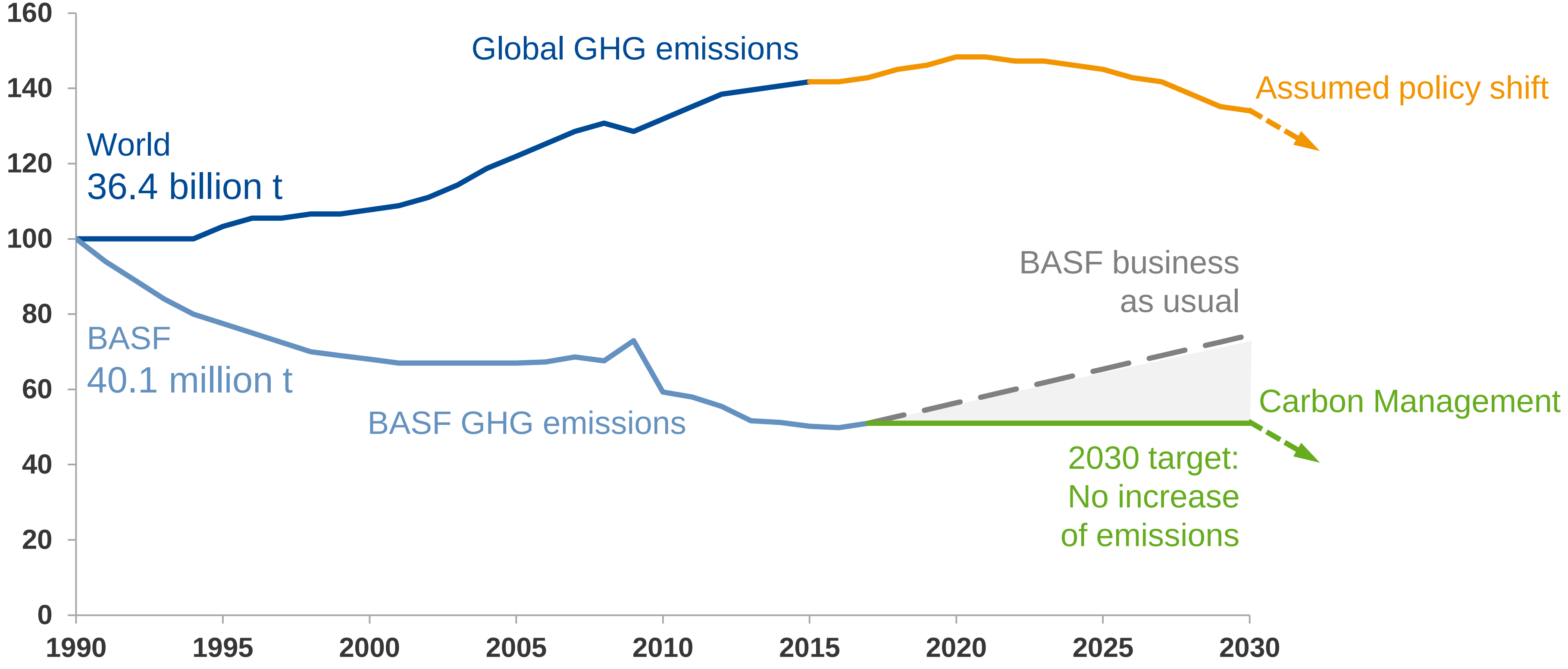
- Activation of CO_2 from steel plant (CCU)
- Breakthrough technology for sustainable hydrogen with
  - with low carbon footprint
  - and low energy demand
- Substitution of coal-based carbon

Bode et al., 1. Jahrestagung der GDCh Fachgruppe Chemie Oct. 06, 2016 und Energie, 6.-7.10.2016 in Jena

Our target: CO_2-neutral[1] growth until 2030

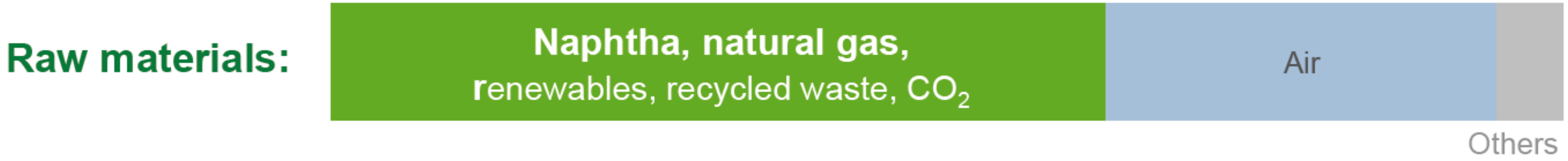
Absolute GHG emissions

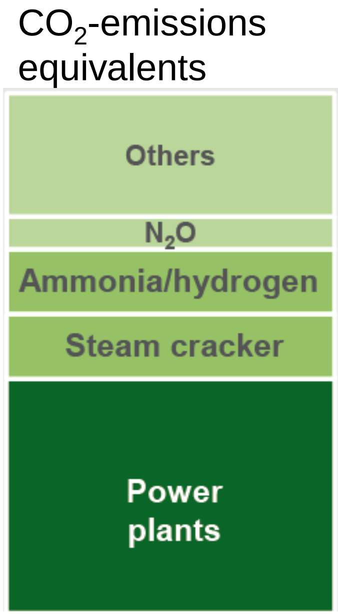
Indexed (1990 = 100)



[1] BASF operations excluding the discontinued oil and gas business. The goal includes other greenhouse gases according to the Greenhouse Gas Protocol, which are converted into CO_2 equivalents.

BASF's C-balance calls for CO_2-avoidance and renewable energy





Process optimization, energy management, N_2O decomposition

Clean hydrogen research, e-furnace research, clean olefins research

Purchase of renewable energy

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Towards a new clean hydrogen production technology

			Direct CO_2 emissions in kg CO_2/kg hydrogen	Minimum energy demand in kJ/mol hydrogen*
State-of-the-art	Steam reforming of natural gas	$CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$	8.85	27
Option 1	Water electrolysis	$2H_2O \rightarrow 2H_2 + O_2$	0	286
Option 2	Methane pyrolysis	$CH_4 \rightarrow 2H_2 + C$	0	37

Water electrolysis and methane pyrolysis yield clean - CO_2-free – hydrogen,
but only in case of non-fossil electric heating

Dr. Andreas Bode, BASF Research Press Conference on January 10, 2019

* Standard reaction enthalpy as approximation

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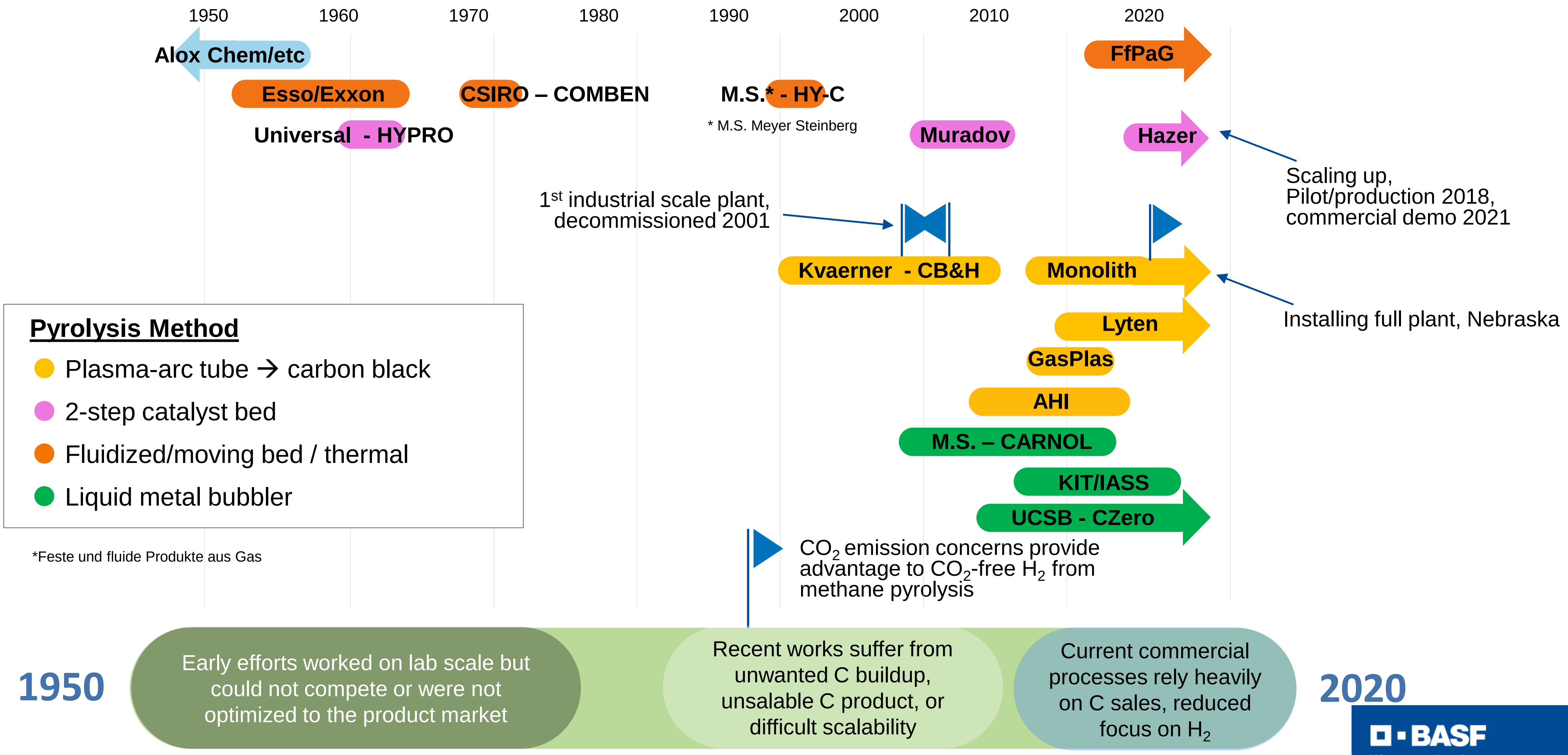
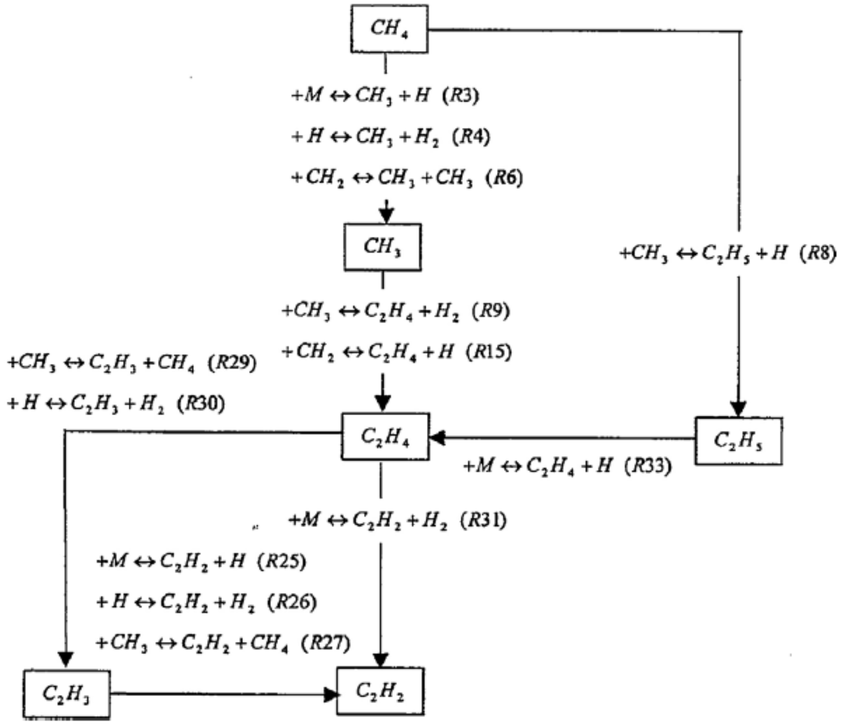
Several projects since 1900



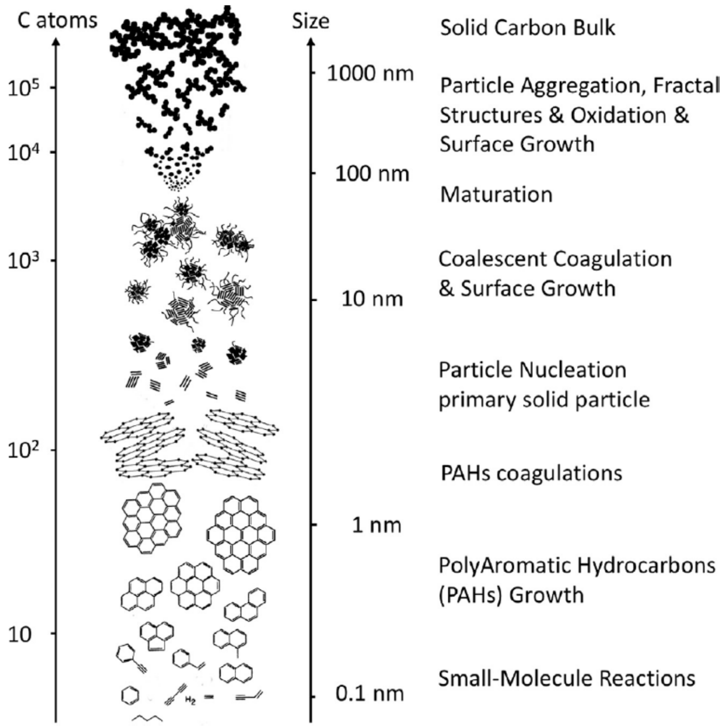
1. Jahrestagung der GDCh Fachgruppe Chemie und Energie, 6.-7.10.2016 in Jena

Methane pyrolysis in thermal plasmas (I): plasma is only the heat source for thermal decomposition

- Hüls acetylene process: in operation since 1940th
- Kvaerner: industrial plant operated ca 2000, for carbon black production
- Monolith: industrial plant to be commissioned 2020, for carbon black production



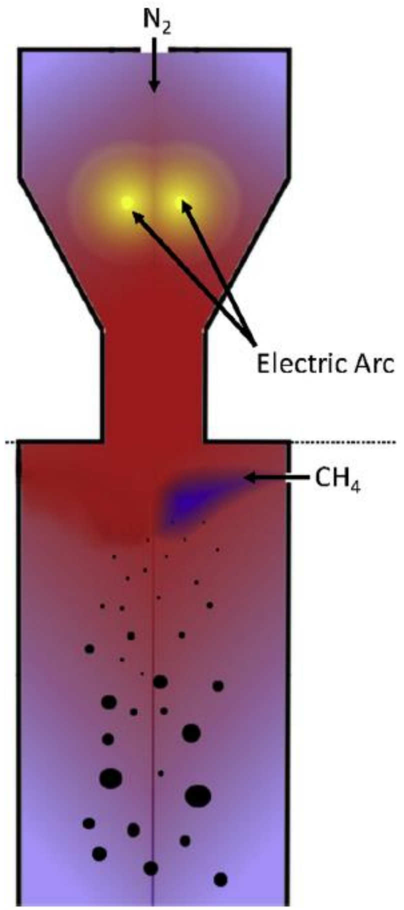
Fincke et al., *Plasma thermal conversion of methane to acetylene*, Plasma Chemistry and Plasma processing, Vol. 22 (1), 2002



Gautier et al., *Direct decarbonization of methane by thermal plasma for the production of hydrogen and value-added carbon black*, International journal of hydrogen energy, 42, 2017, 28140 – 28156

Methane pyrolysis in thermal plasmas (II): plasma is only the heat source for thermal decomposition

- Opportunities
  - high conversions and selectivities close to equilibrium feasible
  - heating technically proven
- Challenges and limitations of thermal plasmas
  - narrow carbon black specifications difficult to meet
  - high temperatures impede heat integration and limit thermal efficiency



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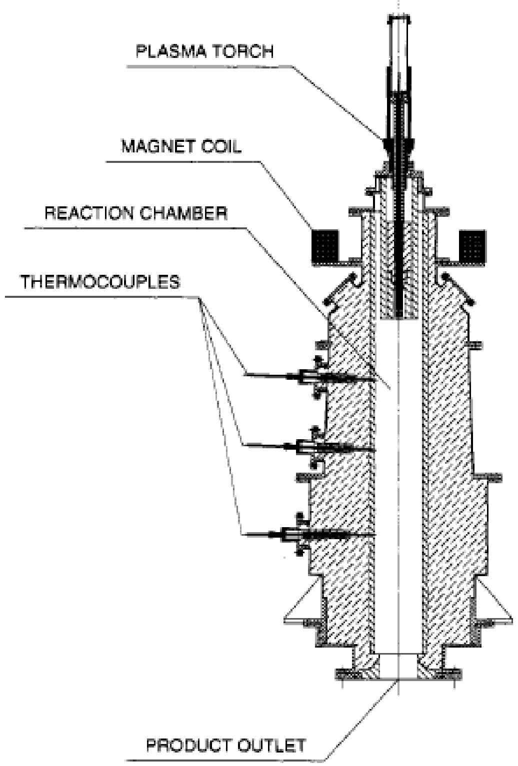


Bakke et al. Pure & Appl. Chem., Vol. 70, No. 6, pp. 1223-1228,1998L; A.N. Wrernes, 0. Raaness, S. Lynum, “Carbon Black and Hydrogen direct from hydrocarbones”, *4th European Congress on*

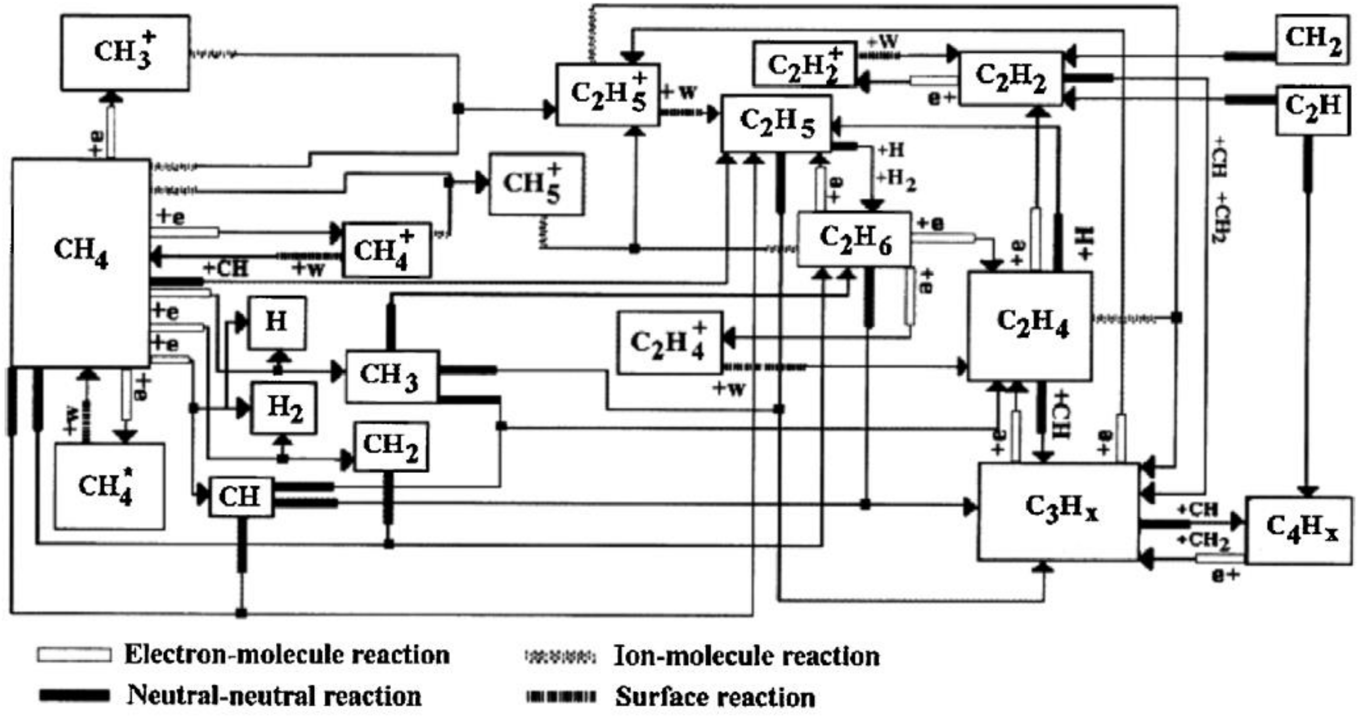
Non-thermal plasmas for methane pyrolysis: a variety of newly emerging approaches for CO_2-free hydrogen

NT-plasma sources

- Microwave (MW)
- Gliding arc (GA)
- Dielectric barrier discharge (DBD)

From process development point of view NT-plasma reactors must

- provide full conversion
- permit sufficient residence time for dehydrogenation and nucleation
- allow narrow carbon specification



Yang et al. , *Direct non-oxidative methane conversion by non-thermal plasma: experimental study*, Plasma Chem, Plasma Process, 23, 2003, 283-296

Warm microwave and gliding arc plasmas with a thermal decomposition contribution appear promising routes to hydrogen generation

Methane pyrolysis is not new:

Several projects initiated, but no commercial realization & still broad technological field

Thermal non-catalytic (fixed/moving/fluidized bed) since 1960's	+ no deactivation + pure C product	- high temperature - heat efficiency, inhomogeneity
Catalytic (fixed/moving/fluidized bed) since 1990's, today e.g. Hazer Group (AU)	+ lower temperature, material of construction + scalability	- C product impure - Catalyst deactivation - Catalyst cost, inerting
Liquid metal/salt Since 1990's	+ good heat transfer + no blocking + catalytic function too	- corrosion - loss of metals/salts - C product impure
Plasma (thermal/non-thermal) since 1990's, today e.g. Monolith	+ flexible reactors, fast on/off + known technology + no deactiv.	- low energy efficiency - limited scalability - broad C quality

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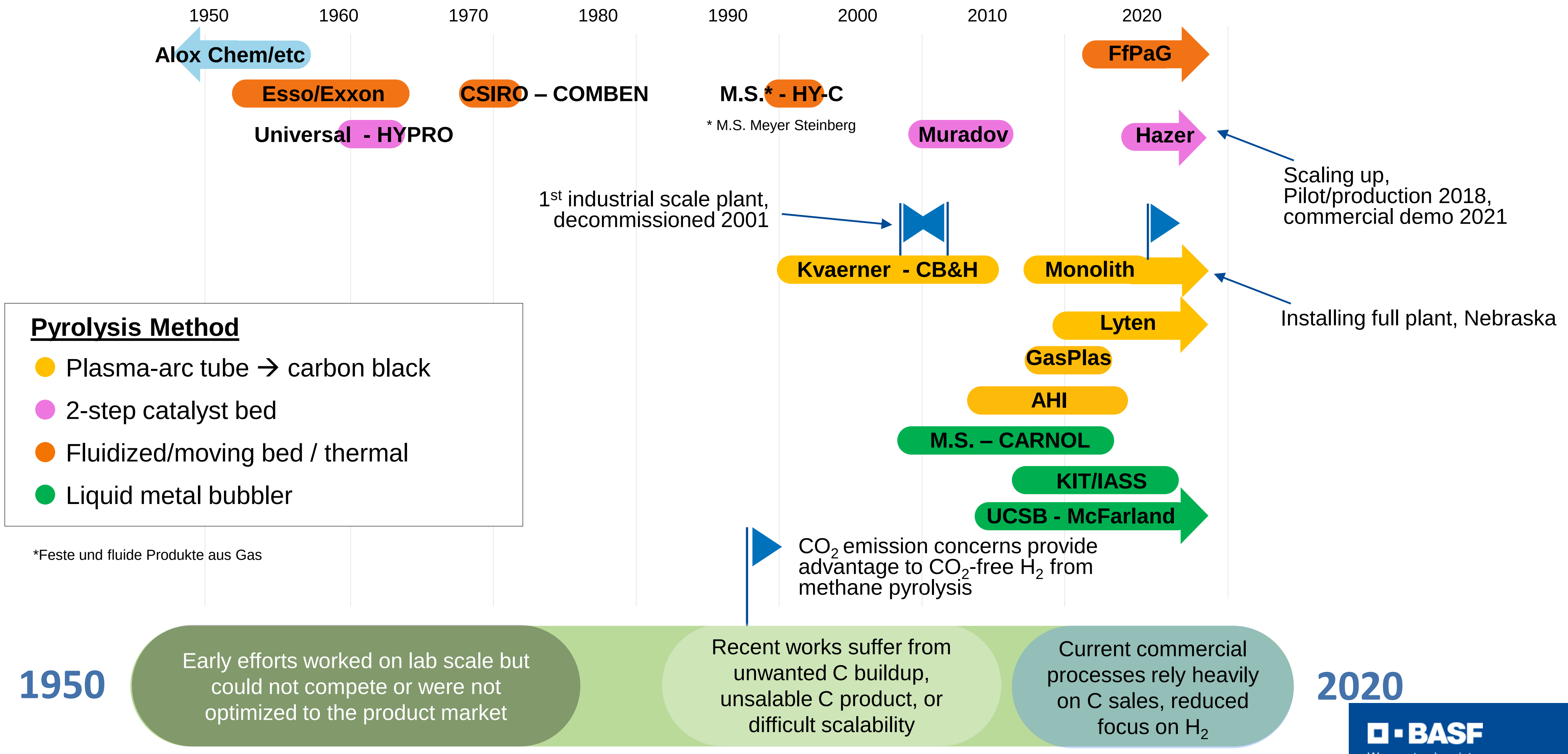
Several projects since 1900



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Summary

- Methane pyrolysis is attractive for CO_2-free hydrogen and high-purity carbon as valuable by-product.
- The chemistry is well known, but the process is not – many processes have significant differences in efficiency, cost, and product
- Historical efforts focused on H_2 *OR* C, but couldn’t compete, renewed interest once CO2 is considered
- More recent efforts, economics w/o CO2 credit require C sale, removal and carbon value is a hurdle. Targeting high value carbon, often H2 is left behind
- Broad technological field approaching commercial realization, but no clear winner. Challenges are process specific, likely many routes will co-exist

Project outlook – methane pyrolysis for clean hydrogen

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1st commercial unit

Pilot unit*

Test of reactor design and carbon outlet

Second R&D project*

Proof of concept for reactor design and carbon outlet

Duration ~3 years

R&D project

Lab-scale proof of concept and sample production

2019

2025

Second R&D project with

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* Government funding will be necessary due to high technological and commercial risk

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